

## X-RAY ANALYSIS OF THREE SERIES OF ALLOYS.

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### SYNOPSIS.

*Crystal structure of three series of alloys* has been determined by Hull's method of x-ray analysis, using sheets of collodion or zapon in which the filings or powders to be investigated were embedded.

The *Fe-Ni* and *Fe-Co* series of pure binary alloys were each found to be solid solutions of one metal in the other with a single region of transition at 22-30 per cent. Ni and at 80-90 per cent. Co respectively. This means that Fe atoms can be substituted for up to 70 per cent. of the Ni atoms in the face-centered Ni lattice and Co atoms can be substituted for up to 80 per cent. of the Fe atoms in the cube-centered Fe lattice without changing the crystal structure. No evidence of a compound  $\text{Fe}_2\text{Ni}$  was obtained.

*Fe-Ni* alloys develop the cube-centered form when made magnetic by chilling in liquid air.

The *Cu-Zn* series of alloys form solid solutions of Zn in Cu up to 47 per cent. Zn, then change first to the cubic, then to the rhombohedral, and finally to the hexagonal form typical of Zn. These changes correspond roughly with changes in the hardness curve. The *effect of annealing* was not appreciable.

IN the past few years much work has been done by x-ray analysis on the crystal structure of those elements which are obtainable in pure solid form at room temperature, and of many of the simpler salts and oxides.

The question arose whether this same method might not be useful and enlightening when applied to alloys.

When a compound of elements of very different atomic weights is examined by x-rays, the diffraction pattern obtained is that of the crystal structure of the heavy element alone, the intensities of the lines of this pattern being modified by the position of the atoms of the light element. This often makes the interpretation of the diffraction pattern, in terms of the complete crystal structure of the compound, extremely difficult. And the complete interpretation of the structure of a compound containing three or more elements is, in the present state of our knowledge and experience, often almost impossible, even though the x-ray diffraction pattern may be perfectly definite.

For this reason we started with very simple and well-known series of binary alloys of metals whose atomic weights differed from one another

only a little, so that we could be sure that they would both reflect x-rays in nearly equal amounts.

We used the Hull method<sup>1</sup> of x-ray analysis. Instead of powders we usually took fine filings, as many of our alloys were not brittle enough for powdering. The samples were prepared by mixing the filings with collodion or zapon and drying the paste to a thin sheet on glass. Such a sheet or film could be readily peeled off when dry and had the advantage of containing very little foreign material, and that little amorphous. Being composed of the light elements C, H, O, etc., quite transparent to x-rays, such a film, when placed in a narrow beam of x-rays, produces very little fogging.

The following data cover work done on nickel-iron, cobalt-iron, and copper-zinc alloys.

#### NICKEL-IRON ALLOYS.

Iron and nickel are known to form an unbroken series of solid solutions of all compositions from 100 per cent. iron to 100 per cent. nickel, though it has been suggested<sup>2</sup> that a compound may exist at 34.45 per cent. nickel ( $\text{Fe}_2\text{Ni}$ ). As can be seen below, our work gave no indication of such a compound. The samples used in our work were prepared by the fusion of pure Swedish iron and pure nickel in a hydrogen resistance furnace. They therefore contained no carbon, and the percentage of other impurities was very low.

The crystallographic structure of alloys of different composition was determined, as shown in Table I.

TABLE I.

*Nickel-Iron Alloys.*

| Per Cent. Ni. | Structure as Shown by X-ray Diffraction Patterns. |
|---------------|---|
| 0             | Centered cubic alone.                             |
| 10            | " " "   |
| 15            | " " "   |
| 20            | " " "   |
| 22            | " " "   |
| 25            | Centered cubic plus face-centered cubic.          |
| 27            | " " " " " "                                       |
| 30            | Face-centered cubic alone.                        |
| 50            | " " " "   |
| 75            | " " " "   |
| 100           | " " " "   |

There is no indication of a change in structure at 34 to 35 per cent. Ni, the composition of invar.

<sup>1</sup> A. W. Hull, *Phys. Rev.*, 10, 661, 1917. *J. A. C. S.*, 41, 1168, 1919.

<sup>2</sup> Chevenard, *Rev. de Metallurgie*, 11, 841. Weiss, *Tran. Faraday Soc.*, 8, 149. Weiss & Foex, *Arch. des Sc. Phys. et Nat.* (4), 31, pp. 4 and 89.

Fig. 1 shows the equilibrium diagram determined thermally as given in the circular issued by the Bureau of Standards: "Invar and Related Nickel Steels," with a small addition below it showing the structure as determined by x-ray analysis. The agreement is fair, and might be better below 22 per cent. Ni if the x-ray method were capable of detecting very small percentages of a crystal form. That is to say, though the x-ray pictures show a pure centered cubic form at 20 per cent. Ni, there might be one or two per cent. of the face-centered cubic form present. A ten to one artificial mixture of iron and nickel (*i.e.*, centered cubic with face centered cubic structure) showed both forms quite distinctly, but we have not tested mixtures containing smaller percentages of nickel.

Fig. 2 shows the diffraction patterns as photographed from some of the alloys of this series.

These patterns prove that nickel atoms can be substituted for iron atoms in the iron (centered cubic) crystal lattice until about 20 per cent. of the iron has been so replaced. On the other hand, iron can substitute for nickel in the nickel face-centered cubic lattice to a much greater extent; *i.e.*, until about seventy per cent. of the nickel atoms have been replaced by iron atoms. These replacements are possible because the atomic volumes of iron and nickel are nearly the same, iron being 7.2, nickel 6.7, and the shapes of the atoms are nearly enough alike to make substitution possible with little strain of the intra-atomic forces. Some of the photographs show, along the edge, a scale which we occasionally used. It consisted merely of a thin sheet of molybdenum in which slots were cut at spacings calculated so as to read Ångstroms direct on the photograph.

It will be noted that the transition from the centered cubic form to the face-centered cubic form takes place between 22 and 30 per cent. Ni. This is also the region in which some of the physical properties of the ferro-nickels have maxima or minima, such as hardness,<sup>1</sup> tensile strength,<sup>1</sup> magnetic saturation intensity<sup>2</sup> and hysteresis losses,<sup>3</sup> though most of the properties investigated<sup>4</sup> have maxima or minima at about 35 per cent. Ni,<sup>4</sup> this being the reason for the assumption of the compound Fe<sub>2</sub>Ni.

The density, electrical resistance and elasticity of ferro-nickels in this transition range (20 to 30 per cent. Ni) varies with the history of the

<sup>1</sup> Circular of the Bureau of Standards, No. 58 (Invar and Related Ni steels).

<sup>2</sup> Yensen, Journ. A. I. E. E., April, 1920, p. 396.

<sup>3</sup> Honda, Sci. Reports. Tohoku Invs. University, 7, p. 59, 1918.

<sup>4</sup> Ingersoll & Others, PHYS. REV., 16 (2), 126.

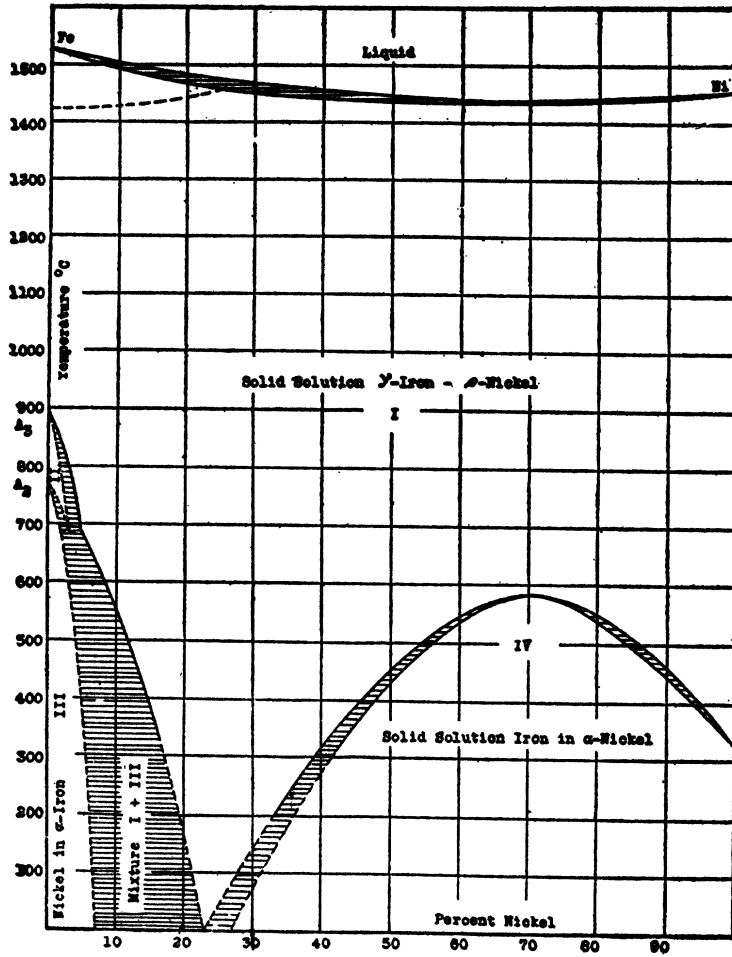


FIG. 1.—The iron-nickel equilibrium diagram

Structure by X-Ray Analysis

|                   |         |                     |
|-------------------|---------|---------------------|
| centered<br>cubic | Mixture | Face-centered cubic |
|-------------------|---------|---------------------|

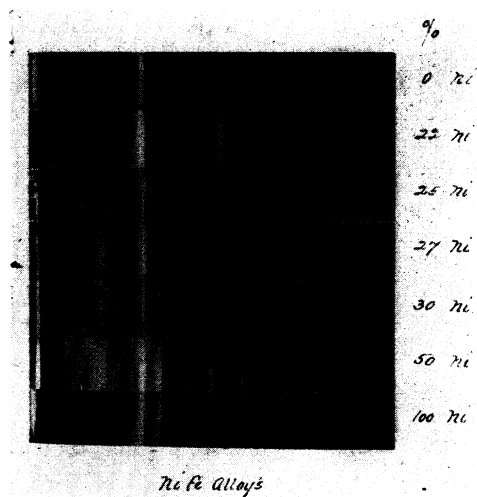


Fig. 2.



Fig. 3.

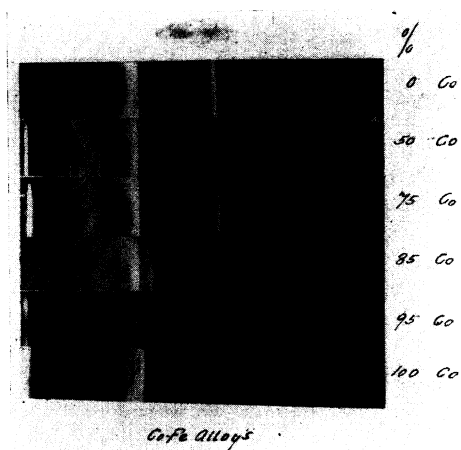


Fig. 4.

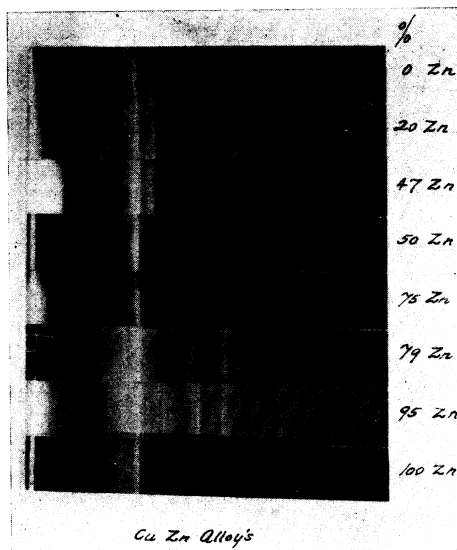


Fig. 6.

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specimen,<sup>1</sup> and this effect is also very marked with the magnetic properties.<sup>2</sup> The magnetic transformation curves as determined by Hegg<sup>3</sup> and others show a wide difference between the temperature of transformation on heating and on cooling for alloys between twenty and thirty per cent. nickel. If the alloys are free from carbon and manganese, both these curves lie above room temperature, and the alloys are, therefore, always magnetic at room temperatures. But if a few tenths of a per cent. of carbon be present, or a little manganese, these transformation curves are lowered so that it is possible to obtain an alloy that will be at room temperature, either magnetic or non-magnetic; *i.e.*, the irreversible alloys. If it has been cooled from a sufficiently high temperature it will be non-magnetic. If warmed from a low temperature, it will be strongly magnetic.

The alloys which were used for the photographs shown on Fig. 2 were all apparently so free from carbon, etc., that their transformation curves both lay above room temperature, as they were all strongly magnetic. But I obtained from the Bureau of Standards a sample of almost entirely non-magnetic nickel steel containing 20.1 per cent. Ni, which I photographed before and after chilling with liquid air. (See Fig. 3.) These photographs were made on the solid samples, since filings were always magnetic. The rod was filed to a wedge and the edge of this wedge was placed just in the beam of x-rays. I made photographs on samples which had been freshly filed down, and then on the same samples etched off slightly with hydrochloric acid, to determine whether there was a change at the surface due to the filing off, sufficient to show on the photographs, but could detect no difference in the pictures. However, on chilling for two or more hours in liquid air, there is, as the photographs show, a marked development of the centered-cubic form which was absent or very faint in the non-magnetic material. This test was made three times, and in every case the centered-cubic structure developed to a considerable extent. As nearly as possible the same surface of the alloy was exposed before and after chilling. The surface remained bright and free from rust or tarnish in two of the cases. In the third, the interval that elapsed between chilling and photographing was so long, due to difficulties with the x-ray apparatus, that a slight tarnish developed. This was wiped off as much as possible with a soft cloth. The penetration of the rays used is probably, for these alloys, sufficient to give

<sup>1</sup> Hopkinson, Proc. of the Royal Society, 48, 1; 50, 121.

<sup>2</sup> Honda, *Idem*.

<sup>3</sup> Archives des Sciences Physique et Naturelles, Vol. 30, p. 15.

the structure at a hundred or more microns depth, so that a very slight surface change would not affect the photograph to any extent.

This development of the cube centered form is interesting. It is an increase of the form characteristic of the stronger and more magnetic component of the alloy, iron, and therefore a decrease in the form (face-centered cubic) characteristic of the weaker and less magnetic component, nickel. Moreover, the centered cubic form is less closely packed than the face-centered, which would account for the change in density found by Hopkinson. Why the specific resistance should decrease, as he found, with an increase of the iron form, is less clear. These photographs would indicate that magnetic properties and crystal structure are closely connected, but it is not to be assumed that the centered cubic structure is necessarily magnetic. Chromium, molybdenum, and tungsten all occur in this system, and their magnetic properties are at best extremely feeble.<sup>1</sup>

It is to be noted that this non-magnetic alloy had a pure face-centered form, whereas the ferro-nickels of about the same composition, shown in Table I. and Fig. 2, which were magnetic, show a cube-centered form, the form that develops on chilling the non-magnetic alloy.

Small amounts of manganese, chromium, carbon, etc., doubtless influence the exact compositions at which the transition from cube-centered to face-centered form occurs. For instance, a sample of nickel steel prepared by Mr. A. W. Merrick, of the General Electric Company, which contained manganese and carbon, showed strong face-centered and weak centered cubic form, though it contained only about 18 per cent. nickel. It was weakly magnetic.

The whole question of magnetism of metals and alloys, including the Heusler alloys, offers a most fascinating field for investigation by x-rays, and I hope later to be able to do some work along these lines. A single Heusler alloy, sent to Dr. Hull by Dr. S. J. Barnett of Carnegie Institution, which was photographed, showed a centered cubic form.

#### COBALT-IRON ALLOYS.

Cobalt and iron, like nickel and iron, form an unbroken series of solid solutions. The atomic volume of cobalt is 6.85, of iron 7.2. The equilibrium diagram as given by Guertler,<sup>2</sup> shows a transformation curve that breaks at about 80 per cent. cobalt. Our photographs (see Fig. 4) show the centered cubic (iron) form for alloys from 0 to 80 per cent. cobalt, then the face-centered form begins to develop, so that at 85 per cent. Co we have both forms together, and above this percentage of

<sup>1</sup> A. W. Hull, The Positions of Atoms in Metals, Trans. A. I. E. E., 1920.

<sup>2</sup> Metallographie, 1 Band, Die Binäre Legierungen, p. 78.

cobalt the face-centered form only occurs. The alloy containing 98 per cent. of cobalt showed a trace of the hexagonal form, but chiefly the face-centered cubic. Pure cobalt crystallizes in both the face-centered and the hexagonal forms.<sup>1</sup>

TABLE II.

*Cobalt-Iron Alloys.*

| Per Cent. Co. | Crystal Structure by X-ray Diffraction Patterns. |
|---------------|--|
| 0             | Centered cubic.                                  |
| 20            | " "  |
| 30            | " "  |
| 50            | " "  |
| 75            | " "  |
| 80            | " "  |
| 85            | Mixture.   |
| 90            | Face centered cubic.                             |
| 95            | " " "  |
| 98            | " " " plus trace of hexagonal.                   |
| 100           | " " " " hexagonal.                               |

The physical properties of the iron-cobalt alloys do not seem to be connected with this crystal structure. Yensen<sup>2</sup> has done a vast amount of work on the magnetic properties, and finds that the magnetic permeability increases with increase in the per cent. of cobalt, up to 34.5 per cent. cobalt (Fe<sub>2</sub>Co), being at this point about 13 per cent. higher than pure iron, but that further addition of cobalt reduces the permeability. Honda<sup>3</sup> finds that the thermal and electrical conductivity decrease from 0 to 10 per cent. cobalt, increase to 65 per cent., decrease to 90 per cent., and then increase to 100 per cent. cobalt.

COPPER-ZINC ALLOYS.

The atomic volumes of copper and zinc differ rather widely, that of copper being 7.1 and of zinc 9.17. Therefore, only about half of the series forms solid solutions. Table III. shows the crystal structure of the alloys examined, and Fig. 5 the transformation curve for the copper-zinc alloys taken from Guertler,<sup>4</sup> below which has been sketched the divisions into crystal forms as shown by the x-rays. Type IV. of Guertler's diagram does not appear in the x-ray forms, at all. The pattern obtained from the alloys containing 79 and 82 per cent. zinc, agreed very well with the curves, to which we had access, prepared by Drs.

<sup>1</sup> A. W. Hull, *ibid.*  
<sup>2</sup> Trans. Am. Electrochem. Soc., Vol. 32, p. 165.  
<sup>3</sup> Sci. Reports Tohoku Imp. Univ., Vol. 8, p. 51.  
<sup>4</sup> Metallographie, 1. Band, p. 459.



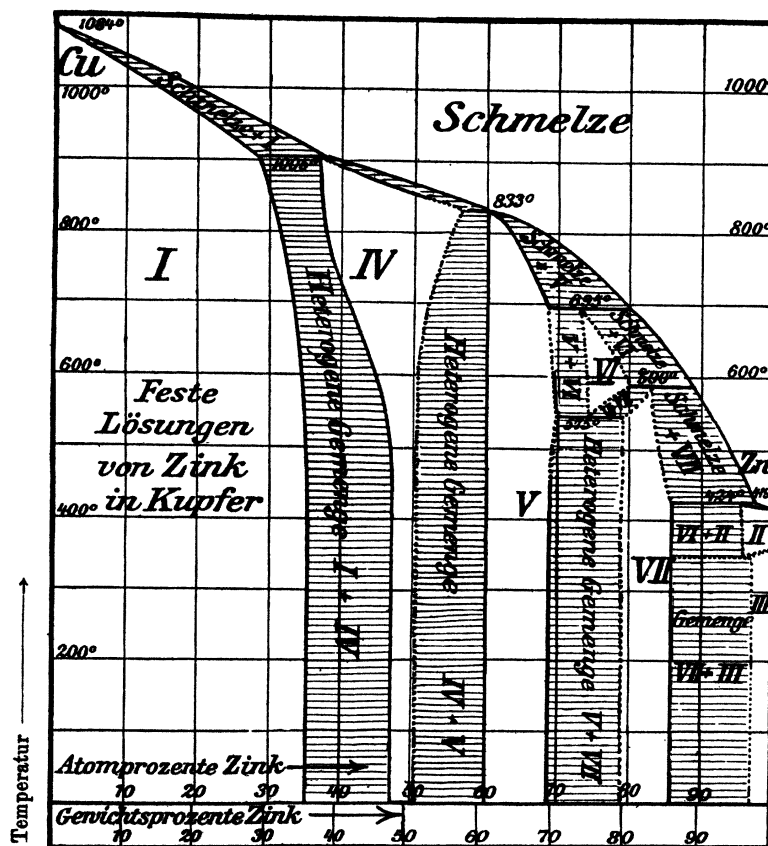


Fig. 189.

Zustandsdiagramm der Kupfer-Zink-Legierungen.

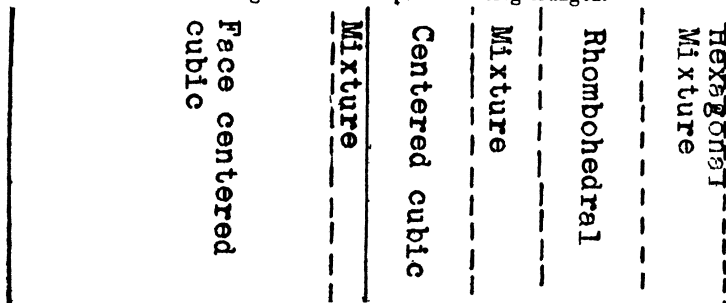


Fig. 5.

Hull and Davey,<sup>1</sup> for the rhombohedral form if taken at an axial ratio of .5. Some of the photographs are shown in Fig. 6.

TABLE III.

| Per Cent. Zinc. | Crystal Structure as Found by X-ray Diffraction Patterns. |
|-----------------|---|
| 00 (pure Cu)    | Face-centered cubic.                                      |
| 20              | " " "   |
| 31              | " " "   |
| 37              | " " "   |
| 47              | Mixture face-centered cubic and centered cubic.           |
| 50              | Centered cubic.   |
| 63              | " "   |
| 69              | Mixture.  |
| 79              | Rhomboidal.   |
| 82              | "   |
| 90              | Mixture rhomboidal and hexagonal.                         |
| 94              | " " " "   |
| 100             | Hexagonal.  |

While there is voluminous literature on the copper-zinc alloys, most of it is confined to the commercial brasses and Muntz metals; *i.e.*, the alloys containing less than fifty per cent. zinc. These are all solid solutions of zinc in copper.

The Lunkenheimer Company has, however, been kind enough to allow me to print the hardness curve shown in Fig. 7 which was deter-

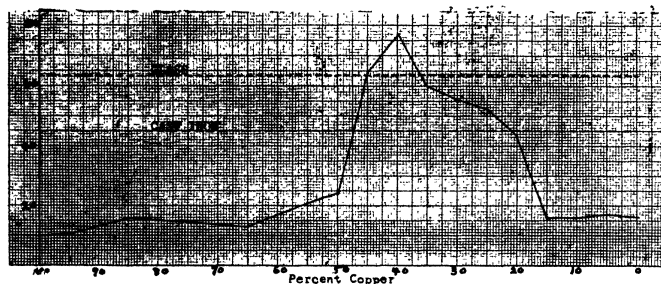


Fig. 7.

mined by Mr. G. K. Elliott, of that Company, with the Shore Scleroscope. This curve agrees roughly with the divisions of crystal forms.

We tried the effect of annealing on a number of samples, but did not find that this treatment caused any change of structure.

Calculating the density of the alloy containing fifty per cent. of each component, which showed pure centered cubic structure, gave a value of 8.17. Maey<sup>2</sup> gives 8.14.

<sup>1</sup> PHYS. REV., Feb., 1921, p. 266.

<sup>2</sup> Zeit. Phys. Chem., 38, 299.

We conclude that this method should be useful in determining the structure of other series of alloys.

Finally, I wish to express my hearty thanks to Dr. A. W. Hull, under whose direction this work was done, for the interest he has shown and for his many helpful suggestions.

RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY, SCHENECTADY, N. Y.

April 19, 1921.

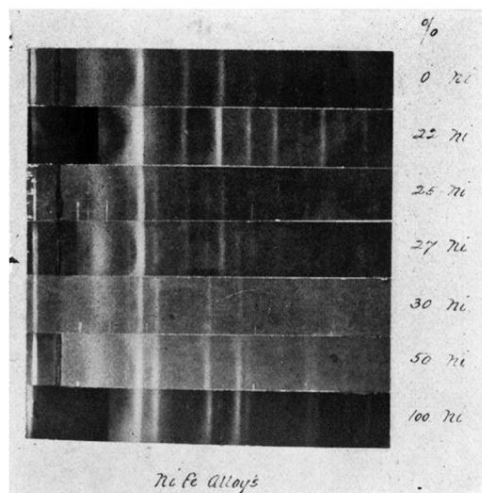


Fig. 2.

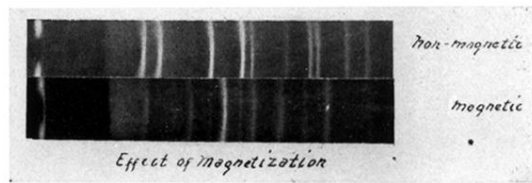


Fig. 3.

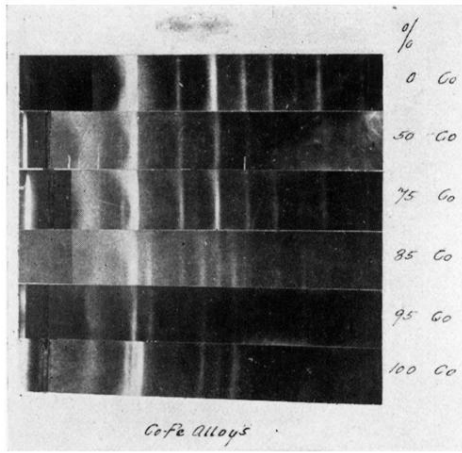


Fig. 4.

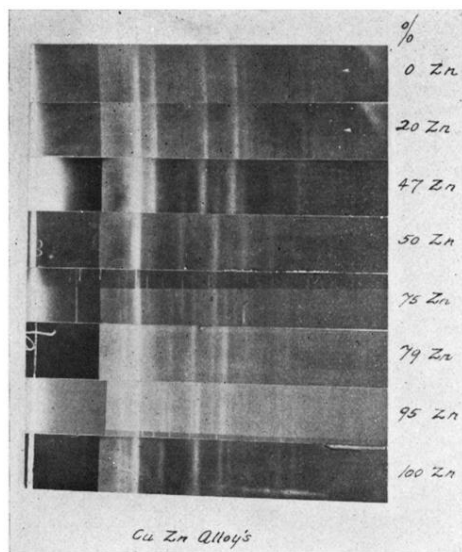


Fig. 6.

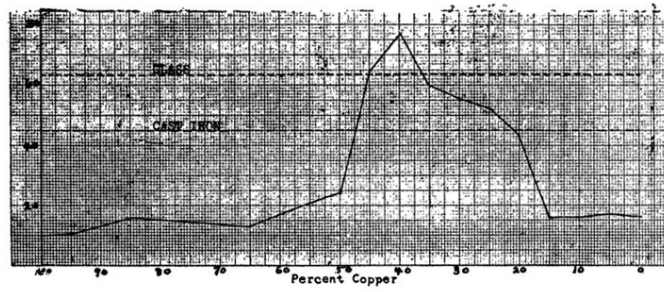


Fig. 7.